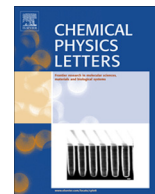


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Reprint of: Ultrafast photoinduced electron transfer in conducting polymer–buckminsterfullerene composites

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ABSTRACT

We report time-resolved photoinduced absorption and time-resolved photoconductivity in conducting polymer- C_{60} composites. Photoinduced electron transfer occurs at times <1 ps. Two subgap features are observed in the photoinduced absorption of pure poly (3-octylthiophene) (P3OT); these form earlier than 1 ps and decay with $\tau < 5$ ps. P3OT mixed with C_{60} shows similar spectral features at early times (<1 ps); however, a new spectrum evolves after ≈ 1 ps as a result of electron transfer from P3OT to C_{60} . Ultrafast photoinduced electron transfer improves the quantum efficiency for photogeneration of charge carriers; in the ps domain the photoconductivity of the conducting polymer host is enhanced by more than an order of magnitude upon mixing in a few percent C_{60} .

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1. Introduction

The observation of reversible, metastable, photoinduced electron transfer from conducting polymers onto buckminsterfullerene was recently reported [1]. Photoinduced absorption and photoinduced electron spin resonance data demonstrated the formation of the charge-separated state [1]. The quenching of the luminescence intensity, the reduction of the luminescence lifetime, and the quenching of triplet formation in the conducting polymer component imply ultrafast photoinduced electron transfer in the composites [1,2]. Ultrafast photoinduced charge transfer from dimethylaniline onto C_{60} has been seen in solution studies. In this case, the back-transfer processes are rapid, with recombination in the picosecond time scale [3].

The photoinduced charge transfer process has been utilized in semiconductor polymer- C_{60} bilayer heterojunctions to fabricate photodiodes and photovoltaic devices [4]. When illuminated, the devices exhibit a large photoresponse as a result of photoinduced electron transfer across the heterojunction interface from the semiconducting polymer (donor, D) onto C_{60} (acceptor, A). Since, charge transfer takes place on the subpicosecond time scale (≈ 1000 times faster than the radiative and/or nonradiative decay of photoexcitations [2]), the quantum efficiency for charge transfer and charge separation is near unity. Such DA heterojunctions are, therefore, of interest because they provide a rational molecular approach to potentially high efficiency photovoltaic cells that could be implemented in large areas.

Although the proof of photoinduced electron transfer from conducting polymers onto buckminsterfullerene is unambiguous, the

time scale for charge transfer has not been established through direct measurements. The demonstration that the luminescence is quenched, and the associated luminescence decay time reduced, is a strong indication of fast electron transfer. However, the luminescence intensity can be affected in other ways, such as by creation of non-radiative decay channels [5]. Thus, it is important to establish directly the time scale for photoinduced electron transfer from conducting polymer to C_{60} to verify if the quantum efficiency is indeed of order unity.

We have now successfully addressed the issue of the time scale of electron transfer through subpicosecond photoinduced absorption and picosecond transient photoconductivity measurements on poly (3-octylthiophene) (P3OT) and on P3OT/ C_{60} composites. P3OT and P3OT mixed with C_{60} show similar spectral features at early times (<1 ps); however, a new spectrum evolves in the composite after approximately 1 ps as a result of photoinduced electron transfer from P3OT to C_{60} . The ultrafast photoinduced electron transfer improves the quantum efficiency for photogeneration of charge carriers; in the picosecond time domain, the photoconductivity of the P3OT host is enhanced by more than an order of magnitude upon mixing in a few percent (wt/wt) C_{60} . We conclude that photoinduced electron transfer from conducting polymer to C_{60} occurs at times of less than 1 ps with the rate limiting step probably being the diffusion of the excited electron–hole pair on the P3OT.

2. Experimental methods

For the subpicosecond photoinduced absorption (PIA) experiments, we use a four-prism, dispersion compensated, colliding pulse mode-locked laser [6] to generate a 96 MHz train of 80 fs pulses at 2.01 eV. The pulses are amplified in a six-pass bowtie amplifier [7] pumped at 8 kHz by a copper vapor laser. This pro-

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duces 100 fs pulses with typical energies of 6 to 8 μJ per pulse. Twenty percent of the output is split off to use as a pump, with the remainder focused with a 10 cm radius spherical mirror into a 3 mm cell of flowing ethylene glycol to produce a white light continuum. Due to dispersion in the ethylene glycol, the white light probe pulse acquires a 50 fs/ 100 nm chirp. The pump beam and the continuum (probe) beam are both horizontally polarized. The continuum beam is passed through a low pass filter with a cutoff energy of 2.1 eV, then split into a probe beam and a reference beam. The pump beam is passed through an optical delay line and focused on the sample to a 0.4 mm² spot overlapping the probe beam (focused to a 0.1 mm² spot). The reference beam is focused on the sample at a spot spatially separated from the pump beam spot. The probe and reference beams are then collected and imaged onto two vertically separated regions of a two-dimensional CCD array. The transmitted spectrum of the probe beam is accumulated during a one second exposure of the CCD array and normalized by the spectrum of the reference beam (accumulated during the same exposure). The differential transmission ($-\Delta T/T$) is calculated by subtracting the normalized spectrum with the pump on from the normalized spectrum with the pump off, and dividing by the normalized spectrum with the pump off. Background spectra were taken by blocking the probe and reference beams and accumulating one spectrum with the pump on, and one with the pump off. Possible effects from luminescence, dark current, and stray light are then corrected for by subtracting the background from the corresponding spectrum after each accumulation.

The transient photoconductivity (PC) measurements are made using the Auston microstripline technique, as described previously [8]. One side of the microstrip is biased with 200 V DC, and the other connected to a PAR 4400 boxcar system fitted with a Tektronix S-4 sampling head. The boxcar is triggered with the light pulse via a photodiode. Excitation pulses are obtained from a PRA LN105A dye laser pumped with a PRA LN1000 N₂ operated at 3–5 Hz. The transient PC data are normalized to an incident photon flux of approximately 3×10^{15} photons/cm² per pulse. The

pulse width is 20–30 ps with an energy of 2 μJ /pulse at 2.9 eV. The temporal resolution of the detection system is approximately 50 ps. Both the PC and the PIA is done with the sample under vacuum (10^{-6} Torr) at 300 K.

The polymer and polymer-C₆₀ samples were made as described previously [2]. The solutions were drop cast onto sapphire substrates for photoinduced absorption and alumina substrates for photoconductivity measurements. At low concentrations of C₆₀ (<5%) the films appeared quite uniform. At high C₆₀ content (for example at 1:1 C₆₀ to P3OT) the composite films were clearly phase separated.

3. Results

Linear absorption spectra showed a broadening of the $\pi-\pi^*$ transition in the composite, with a tail extending into the gap. Similar results have been seen previously and attributed to weak admixture of the donor and acceptor wavefunctions and the formation of a DA complex in the ground state [2].

The PIA spectrum at several delay times for P3OT is shown in Fig. 1. The rise time of the absorption is resolution limited (≈ 300 fs) and reaches a maximum at 750 fs. The spectrum has two distinct peaks, one at 1.9 eV and one at 1.3 eV (the oscillations on the low-energy peak are an artifact due to spectral oscillations in the continuum). The rise time of each feature is less than 300 fs. The initial decay time is approximately 1.2 ps; i.e. comparable with the 800 fs decay found for a similar feature in poly (3-methylthiophene) [9] when convoluted with the 300 fs pulsewidth of the continuum pulse.

The results for the P3OT/C₆₀ composite are displayed in Fig. 2. At 750 fs the P3OT/C₆₀ composite spectrum (Fig. 2) exhibits the peak at 1.9 eV superimposed on a broad absorption centered around 1.6 eV. At 1.4 eV the photoinduced absorption is rising, indicating a second peak at lower energy. Within another 750 fs, the spectrum has obviously changed. At 1.5 ps delay, the peak at 1.9 eV is nearly gone, and a broad feature at 1.6 eV is dominant. This broad maximum subsequently shifts from 1.6 eV toward the red to ≈ 1.45 eV after 500 ps.

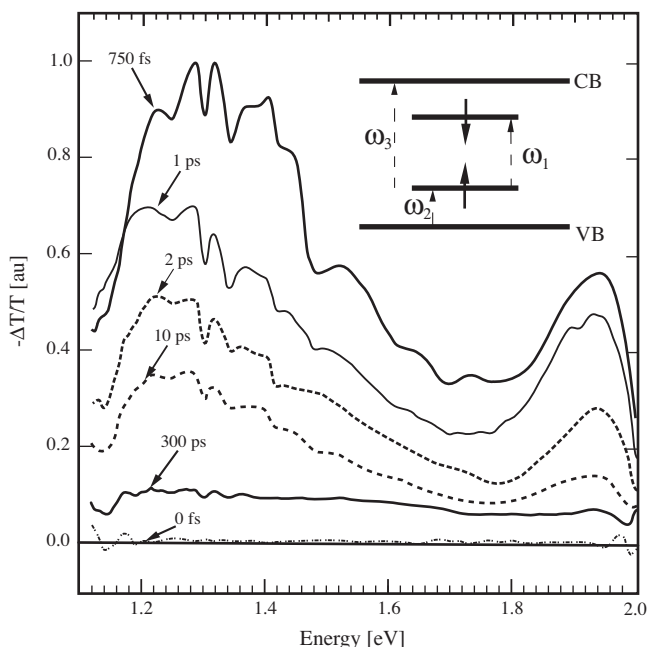


Fig. 1. Photoinduced absorption spectrum of P3OT at various delay times after excitation with a 100 fs, 2.01 eV pump pulse. The inset shows the electronic structure of the neutral bipolaron exciton.

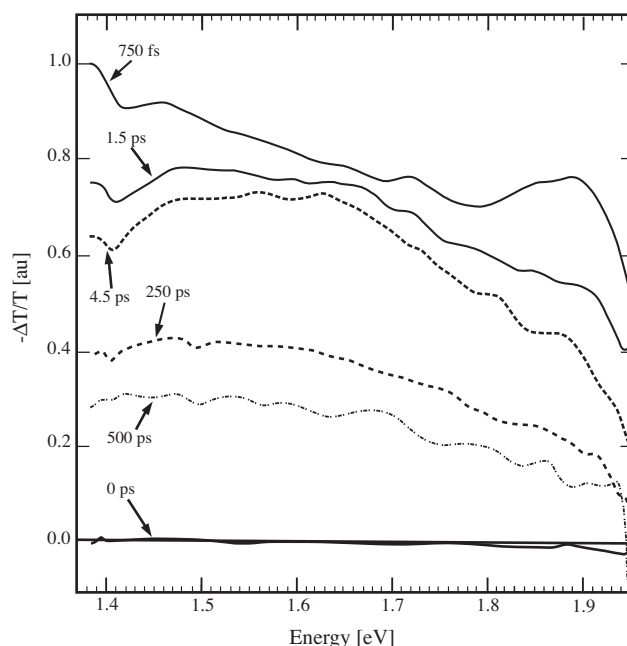


Fig. 2. Photoinduced absorption spectrum of the P3OT-C₆₀ composite (1:1) at various delay times after excitation with a 100 fs, 2.01 eV pump pulse.

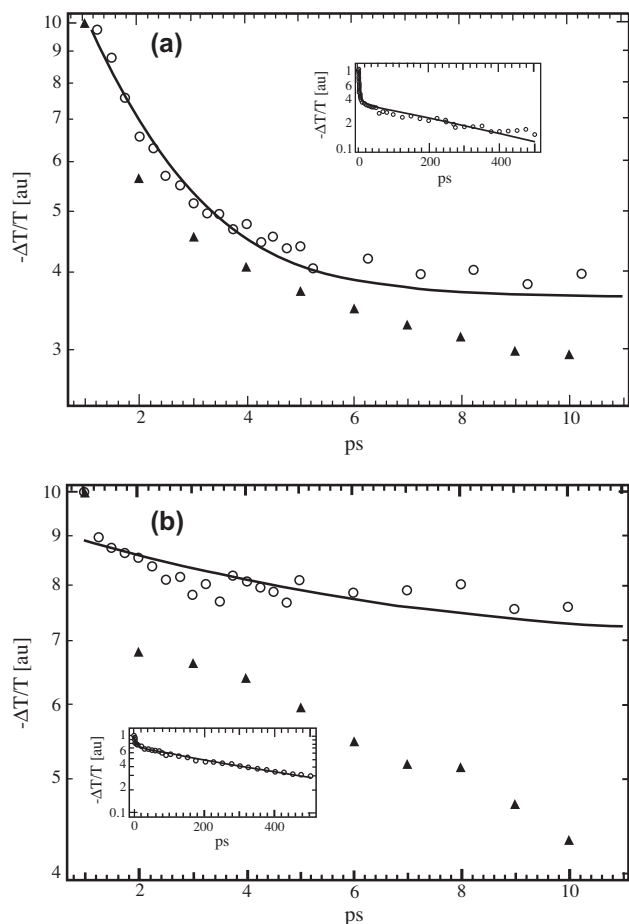


Fig. 3. Time decay of the photoinduced absorption; (a) 1.9 eV and (b) 1.6 eV for P3OT (solid triangles) and P3OT-C₆₀ (open circles). The insets show the decay of the P3OT-C₆₀ spectrum out to 500 ps. The solid lines are fits to double exponentials with the following time constants: (a) $\tau_1 = 1.4$ ps, $\tau_2 = 450$ ps. (b) $\tau_1 = 5.8$ ps, $\tau_2 = 550$ ps.

The decay curves of the PIA features at 1.9 eV (Fig. 3a) and 1.6 eV (Fig. 3b) in P3OT and in the P3OT/C₆₀ composite are compared in Fig. 3. The solid curve in Fig. 3a is a double-exponential (with time constants given in the caption) fit to the data for P3OT/C₆₀. In the composite material, at 1.6 eV, a metastable state is reached within 2 ps following photoexcitation (decreasing by only a factor of 3 after 500 ps; see inset), whereas in P3OT the fast decay persists for a much longer time. At 1.9 eV, the initial decay of the two materials is quite similar. At this energy, the transition from fast to slow decay occurs at ≈ 10 ps. The longer-lived component in the composite material is dominated by the broad feature centered at 1.6 eV.

Fig. 4 displays the time-resolved transient photocurrent (biasing electric field of 2×10^4 V/cm) of a P3OT film containing 5% C₆₀ and a pure P3OT film upon photoexcitation at $\hbar\omega = 2.9$ eV; the addition of 5% C₆₀ to P3OT results in an enhancement of the photocurrent by nearly an order of magnitude. The rise time is limited by the temporal resolution of the detecting system (approximately 50 ps). The C₆₀ serves to increase the charged carrier photogeneration efficiency, resulting in the enhancement of the magnitude of the initial photocurrent. This enhancement of the photoconductive response of conducting polymers by C₆₀ appears to be a general feature; as shown in the inset to Fig. 4, similar results are obtained with poly[2-methoxy-5-(2'-ethyl-hexyloxy)-*p*-phenylene vinylene] (MEH-PPV)/C₆₀ composites. For MEH-PPV/C₆₀, the dark current is below the noise level (and is not shown in Fig. 4); the addition of 1% C₆₀ increases the initial photoconductive response

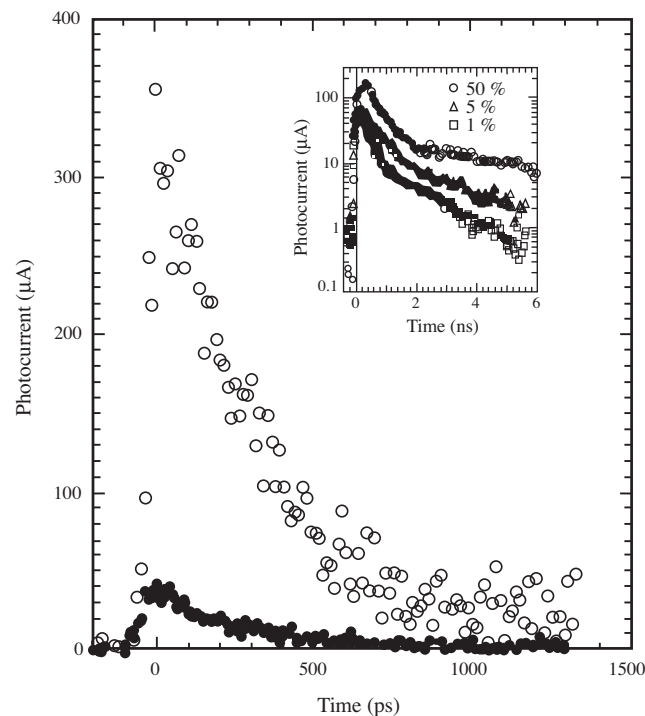


Fig. 4. Transient photoconductivity in P3OT (full circles) and in P3OT sensitized with 5% C₆₀ (open circles). The inset shows the transient photoconductivity for various concentrations of C₆₀ mixed into MEH-PPV, with solid line fits to double exponentials, giving $\tau_1 = 320$ ps, $\tau_2 = 1.9$ ns for the 1% C₆₀; $\tau_1 = 500$ ps, $\tau_2 = 2.5$ ns for 5% C₆₀; and $\tau_1 = 520$ ps, $\tau_2 = 10$ ns for the 1:1 composite.

by nearly two orders of magnitude. Increasing the C₆₀ content causes the photocurrent to continue to increase and results in successively longer lifetimes (see inset). Thus, the charge separation (electron on the C₆₀ and hole on the conjugated chain) serves to prevent recombination, resulting in the enhanced lifetime.

4. Discussion

The photoconductivity data clearly demonstrate the two critical features expected for photo-sensitization via photoinduced electron transfer from P3OT to C₆₀:

- (i) addition of C₆₀ to P3OT enhances the quantum efficiency for photogeneration of charge carriers;
- (ii) Addition of C₆₀ to P3OT inhibits the recombination.

The improved quantum efficiency for charge carrier generation confirms that the electron transfer is ultrafast, competitive even with geminate recombination in the pure P3OT. The enhanced lifetime of the photocurrent is consistent with the metastability of the charge transferred configuration with an electron on the C₆₀ and a hole stabilized as a polaron on the P3OT.

The photoinduced absorption spectrum of P3OT shown in Fig. 1 is consistent with that of a neutral bipolaron (or equivalently, that of a singlet polaronexciton, an exciton stabilized by the chain distortion) with energy levels as sketched in the inset to Fig. 1. Given this electronic structure, we assign the 1.3 eV absorption as the ω_1 transition and the 1.95 eV absorption (from localized state to band states) as the ω_3 transition. Taking the energy gap as 2.1 eV and assuming electron-hole symmetry, the onset of the ω_3 transition should be at approximately 1.7 eV with a peak at approximately 1.9–2 eV due to the broadening of the density of states at the band edge (the energy gap of P3OT is approximately 2.1 eV but the inter-band transition peaks at 2.4 eV for the same reason [10]).

Other possible contributions to the 1.9 eV feature are from electroabsorption [11,12] and thermal modulation of the band edge. We rule out electroabsorption since the enhanced photogeneration of charged carriers in the composite, as evidenced by the increase in the photoconductivity, should induce an enhancement of the 1.9 eV feature in the composite, which is not observed. We have measured the thermal modulation spectrum and find that it does not resemble the PIA spectrum in the picosecond regime. At longer (>100 ps) times, however, the two spectra are much more similar, indicating that thermal effects cannot be ruled out [13].

The uniform decay of the two spectral features in Fig. 1 is consistent with the formation of a neutral bipolaron exciton; both features in the excitation spectrum of P3OT originate from the same excitation. The situation in the composite is more interesting; at 750 ps, the spectrum for the P3OT/C₆₀ composite is similar to that of the pure material. Note however, that the 1.9 eV feature characteristic of the neutral bipolaron exciton is observed only at the shortest times; the spectrum quickly evolves to a single broad peak centered near 1.6 eV. The change in the excitation spectrum after approximately 1 ps sets the time scale for charge transfer. Even at 750 fs, there is partial conversion of the excitation spectrum; the broad absorption over the entire spectral range is clearly observed and the 1.9 eV feature is relatively weak. Thus, we conclude that the photoinduced electron transfer takes place at times less than 1 ps; the persistence of the 1.9 eV feature to approximately 1 ps might well result from diffusion of neutral excitations on the P3OT chains to the vicinity of a C₆₀ acceptor.

After 2 ps, the excitation spectrum is dominated by the broad peak centered at 1.6 eV (shifting to approximately 1.45 eV after \approx 500 ps), in sharp contrast to the spectrum of the pure material. Steady state photoinduced absorption results obtained from the same material show a similar broad peak that is centered at 1.45 eV [2]. Thus, the spectra in Fig. 2 span the relevant time regime from initial photoexcitation on the P3OT to electron transfer, and finally to the steady state photoinduced absorption spectrum. The similarity of the steady state photoinduced absorption spectrum of the P3OT/C₆₀ composite with the spectral changes caused by doping implies the former results from charged excitations, presumably a combination of polarons and bipolarons [2]. Thus, the shift in the broad photoinduced peak from approximately 1.6 eV at \approx 1 ps to 1.45 eV at \approx 500 ps possibly reflects the evolution of the charged species on the P3OT from all polarons to a combination of polarons and bipolarons. Light-induced ESR studies [1,2] provide clear evidence that electron transfer from the P3OT to the C₆₀ occurs in the photoexcited state; two ESR signals are observed with g-values characteristic of (P3OT)⁺ and (C₆₀)⁻, respectively. Hence the formation of a metastable band at 1.6 eV within 1 ps of photoexcitation confirms the ultrafast electron transfer from P3OT to C₆₀.

Examination of the time-evolving spectra in Fig. 2 and the decay curve in Fig. 3a leads to the conclusion that the 1.9 eV peak is gone after a few ps. The residual signal at 1.9 eV, which decays on a much longer time scale (see inset to Fig. 3a), is associated with the charge-transferred configuration; the same long time decay is observed at 1.6 eV (see inset to Fig. 3b). The small difference in the decay curves at 1.9 eV and 1.6 eV ($\tau_2 = 450$ ps and $\tau_2 = 550$ ps, respectively) results from the shift of the spectrum toward lower energies at longer times.

The possibility of non-radiative decay involving positively charged polarons formed by charge-transfer doping in the ground state, as proposed by Morita et al. [14] is ruled out by the electron spin resonance (ESR) measurements [1,2] which show no indica-

tion of the C₆₀ anion signal in the ground state. Further evidence that charge transfer and charge separation occur only upon photoexcitation is provided by the fact that the dark conductivity of the composite is almost identical to that of P3OT alone ($\sigma_d \approx 5 \times 10^{-7}$ S/cm), whereas the photoconductivity of the composite is enhanced by an order of magnitude (Fig. 4).

5. Conclusion

In conclusion, using transient photoinduced absorption spectroscopy and fast transient photoconductivity measurements, we have shown that photoinduced electron transfer from poly(3-octylthiophene) onto C₆₀ occurs on the subpicosecond time scale. The absence of charge transfer in the ground state of the conducting polymer-C₆₀ composites and the subpicosecond electron transfer time (as directly demonstrated by these measurements) imply that C₆₀ is particularly well matched to the electronic structure of conducting polymers. Thus, although any acceptor can successfully perform the role of an electron trap in conducting polymers, the energies of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the magnitude of the electron affinity make C₆₀ a nearly ideal acceptor for use with conducting polymers as weak donors to produce photoinduced charge transfer ($DA + h\nu \rightarrow D^+ + A^-$). Other suitable acceptors should therefore be chosen with similar HOMO, LUMO and affinity energies.

Since the ultrafast electron transfer is nearly three orders of magnitude faster than any competing radiative or nonradiative process, the intrinsic (molecular scale) quantum efficiency for charge transfer and charge separation is indeed close to unity. This high quantum efficiency has important implications for device applications based upon the photoinduced electron transfer; devices such as optical memories, photodiodes and photovoltaic cells [4].

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